Isoprene measurements and emission estimations using the G93 Model during pre-harvest and post-harvest phases of rice paddy fields (*Oryza sativa L.*)

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Abstract

Isoprene is the main biogenic organic compound (BVOC) that contributes to the production of surface ozone (O_3) in the presence of nitrogen oxide (NO_x) and volatile organic compounds (VOCs) as well as sunlight. Surface O_3 is known to be hazardous to human health and to cause crop damage. Various plants are believed to emit isoprene but there is lack of studies on rice plants (Oryza sativa) compared to other plants. In this study, we focus on preliminary investigation into the concentration of isoprene from rice paddy fields pre- and post-harvest. The G93 model for isoprene emission prediction was used to estimate the emission rate of isoprene produced by O. Sativa. The isoprene measurements were conducted over a replica rice field in a low NO_x environment at the University plantation. The amount of isoprene was high during the pre-harvest stage, in the range 0.1 to ~75 ppb.

The isoprene concentrations decreased rapidly during the post-harvest stage down to levels of ~5 ppb. Meteorological factors such as temperature and light intensity controlled the isoprene emissions with $r^2=0.51$, $p=0.02$ and $r^2=0.84$, $p<0.01$ respectively. This study showed that rice plants can be primary emitters of isoprene. Our study provides an early warning of the urgent need to develop policies that manage NO_x emissions if the detrimental effects of rice production on air quality and climate are to be avoided.

Keywords: Isoprene, Biogenic Organic Compound, *Oryza sativa L* and G93 model.

Introduction

Biogenic volatile organic compounds (BVOCs) are emitted from various types of plants widely investigated by researchers in recent decades[3,20-22,29]. Quantitatively, isoprene (C_5H_8) emissions from terrestrial plants are the most important of the non-methane BVOCs (NMBVOCs) with an annual emission of about 400–600 TgC or about 90% of the total NMBVOCs[25] and tropical forest ecosystems are the largest single of isoprene[15]. In recent study, the tropical forest isoprene emissions are much larger than originally thought of up to three times higher in the Amazon rainforest.

Earlier study has also observed that, at the canopy level, tropical oil palm in Borneo emits up to six times higher than tropical rainforest in the region[21]. Isoprene concentration in the atmosphere is believed almost equal to the global emissions of methane from all sources [9,13].

Over decades of research, highly reactive isoprene has shown to contribute significantly to the atmospheric chemistry as they are playing importance roles to the oxidative capacity of the atmosphere[16,27] and secondary organic aerosol formation[14,23,30].

A larger interest on the roles of the isoprene to the tropospheric ozone production under various conditions was widely investigated[5,17]. Isoprene emissions from broadleaf trees and other trees under different plant functional types have been the target of most investigation in past.

Tropical rainforest, which is known as the largest source of isoprene emission has been the target of many investigations particularly in the Amazon, Caribbean, Southeast Asia and Western Africa. A large conversion of tropical rainforest into commercial oil palm plantation in Southeast Asia has prompted a number of preliminary studies to quantify isoprene emission and how it plays role in ozone tropospheric chemistry[12,21].

By far, isoprene emissions investigation from other plant functional types such as grassland category has been very limited.

Rice paddy (*Oryza sativa*), which can be categorized under grassland plant functional type for the estimation of biogenic emissions, has been of interest in recent time due to the massive areas of paddy field in Asia and particularly in

Southeast Asia. Paddy is the second-most important vegetation crop in the world after wheat and Asia is known as the largest producer and consumer of rice[10].

One of the earlier interests on the investigation of isoprene emissions from paddy was from Bao et al[2] . How significant is the isoprene emissions from paddy in the equatorial tropics is less known and certainly warrants the investigation particularly on isoprene fluxes at various stages of paddy growth. The growth and development of the paddy plants involve leaf phenology change and this is expected to change the potential isoprene fluxes.

In this investigation, we focus on the isoprene fluxes at different growth stages of paddy namely during pre-harvest and post-harvest. The investigation also includes the meteorological factors such as temperature and light intensity and how these factors could trigger isoprene fluxes. Finally, G93, a commonly-used model for the isoprene emission rate estimation was used on paddy.

Material and Methods

Isoprene measurements: *In situ* continuous measurement of isoprene was conducted using the portable GC-FID at replica paddy Oryza. sativa (O. sativa) field at The National University of Malaysia (UKM) over the period of 1 month. The field contained 10 plots of rice plant with the area of 25m x 25m, each plot has 5m x 5m area as shown in figure 1. A 10-m long 1/4" ID Teflon sample line was positioned above the paddy field to draw air samples from the inlet to the GC analyser.

The GC system (Synspec GC955) (Synspec b.v, The Netherland) equipped with the FID detector and internal preconcentration tube Tenax® GR as the absorbent. PLOT capillary column CP-Al2O3/Na2SO4 10-m (5-µm film thickness, 0.32-mm ID) was used for the separation. The calibration was conducted using 50 ppb of isoprene standard (MESA, USA) diluted to 40, 20 and 5 ppb in 10 ml canister. A good linear correlation (r^2=0.996) was found for the calibration. Detection limit was estimated to be 0.02 ppb based on replicates of the lowest calibration point. Samples were collected for every 30 minutes' interval depending on the sampling sequence chosen for a particular experiment. Validation for drift check on isoprene was evaluated and observed <2%.

Meteorological measurements: The meteorological data over the sampling site were collected using a WD-2700 Watchdog weather station (Spectrum Technologies, Inc, USA). The weather station measured temperature, humidity, rainfall, wind speed and direction and solar radiation during the measurement period. The weather station was deployed on the roof top of the Centre for Research Institute of Management (CRIM) UKM which is situated approximately 100 m from the paddy field.

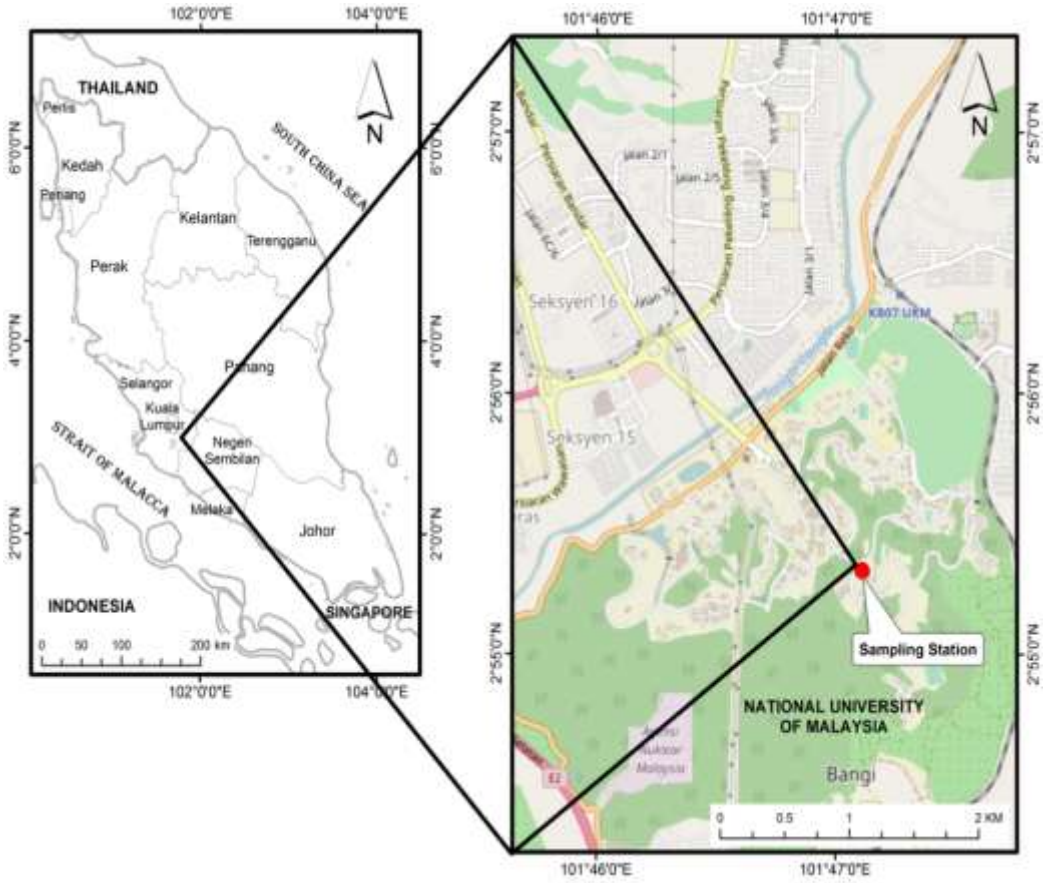

Fig. 1: Sampling location at UKM Campus, Bangi.

Statistical Analysis: Univariate analysis on the relationships between isoprene and light and between isoprene and temperature was examined using Spearman rank correlation. For multivariate analysis, we used principal component analysis (PCA) to elucidate the influences of light and temperature on isoprene. Data used in PCA were composed of 45 collocated measurements and were mean-centred and normalised to one standard deviation prior to the analysis. All statistical analyses were conducted with the statistical computing software "R" (R Core Team, 2014).

Isoprene emission calculations: In this study, we used the G93 model developed by Guenther et al[9] which is an algorithmic expression allowing a quantification of BVOC emissions from various types of vegetation. I (hourly isoprene emission) was estimated by:

$$I = Is \, . \, C_L \, . \, C_T \qquad (1)$$

where I is isoprene emission rate at a temperature T(K) and PAR flux (µmol m^{-2} s^{-1}), Is is isoprene emissions at a standard temperature, Ts (K) and a standard PAR flux (1000 µmol m^{-2} s^{-1}). The factor C_L is defined by

$$CL = \frac{\alpha \, C_{L1} \, L}{\sqrt{1 + \alpha^2 L^2}} \qquad (2)$$

where α (= 0.0027) and C_{L1} (= 1.066) are empirical coefficients that were determined by nonlinear best fit procedures using eucalyptus, sweet gum, aspen and velvet bean emission rate calculation. Equation (2) simulates a nearly-linear increase in isoprene emissions up to a saturation point and is similar to equations which have been used to model the light dependency of photosynthesis. The coefficient α is the initial slope of the curve relating normalized isoprene emission to PAR and is analogous to quantum use efficiency (on an incident light basis). The coefficient C_{L1} is set to force CL equal to 1 at the standard condition of 1000 µmol m^{-2} s^{-1}.

Results and Discussion

Isoprene measurement during pre and post-harvest: The isoprene concentrations measured over *O. sativa* from the 4th November 2017 to the 11th December 2017 (37 days) are shown in figure 2. A strong diurnal cycle is seen with the highest values between 1200 and 1400 local time. The maximum daytime peak values observed are ~70 ppb on 17th November 2017 during the pre-harvest stage. The lowest concentrations (peak <1 ppb) occurred during the night but concentrations more usually were in the range 3 to 11 ppb during the night at the pre-harvest stage. However, the isoprene concentrations decreased during the post-harvest stage.

According to Redeker et al[26] to accurately measure isoprene emissions from rice paddy fields, the fields must be characterized during the vegetative, reproductive and ripening stages. During this pre-harvest phase, the numbers of tillers (or shoots) and plant heights expand very quickly[26].

In the post-harvest phase, the peak values are in the range of ~<5 ppb but some days showed a spike during the daytime with values ranging from ~5 to 10 ppb. This result clearly shows that the concentrations of isoprene are linked to the growth of the rice paddy field. Boa et al showed that large amounts of isoprene (224.21 ug g_{dw}^{-1} h^{-1}) were detected from *Quercus serrata* (*Q. serrata*) paddy fields found in Japan.

Previously, *O. sativa* had not been reported to emit BVOCs, but five kinds of monoterpenes were detected[2]. Our result clearly shows that *O. sativa* can emit large amounts of isoprene.

In this study, the emission rate was higher during the pre-harvest compared to the post-harvest phase (Table 1). Redeker et al[26] showed that the isoprene emitted from *O. sativa* was 3.5 to 11 µg m^{-2} hr^{-1} in a chamber experiment.

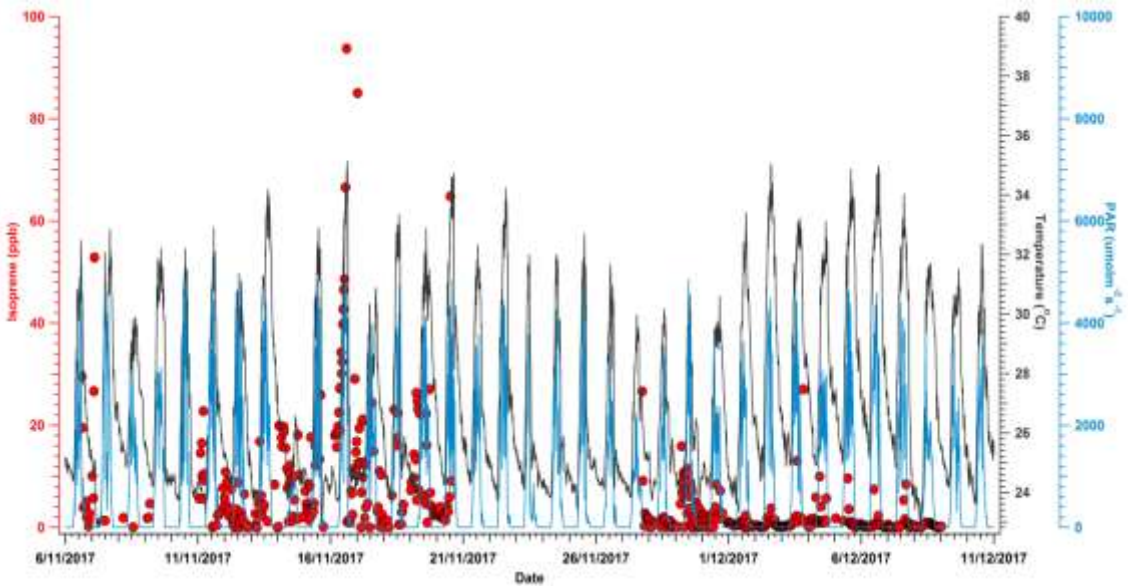

Fig. 2: Concentrations of isoprene and meteorological factors during measurement period.

Table 1
Hourly average concentrations of isoprene during pre-harvest and post-harvest during the measurement period.

Growth	Date	Stdev (±)	min	max	Hourly average isoprene concentration [ppb]	Emission Rate ($\mu g\ g^{-1}\ h^{-1}$)
Pre-harvest	6^{th} – 7^{th} Nov	6.15	0.1	3.22	3.22	0.052
	8^{th}-10^{th} Nov	1.65	0.4	4.66	2.07	
	11^{th} – 16^{th} Nov	13.26	0.3	70.01	10.56	
	17^{th} – 22^{nd} Nov	12.54	0.1	70.25	8.99	
Post-harvest	28^{th} Nov – 1^{st} Dec	5.35	0.1	0.67	0.53	0.013
	2^{nd} - 4^{th} Dec	3.40	0.12	2.01	1.52	
	5^{th} – 7^{th} Dec	1.72	0.12	1.12	0.86	
	7^{th}- 10^{th} Dec	1.30	0.1	0.53	0.58	

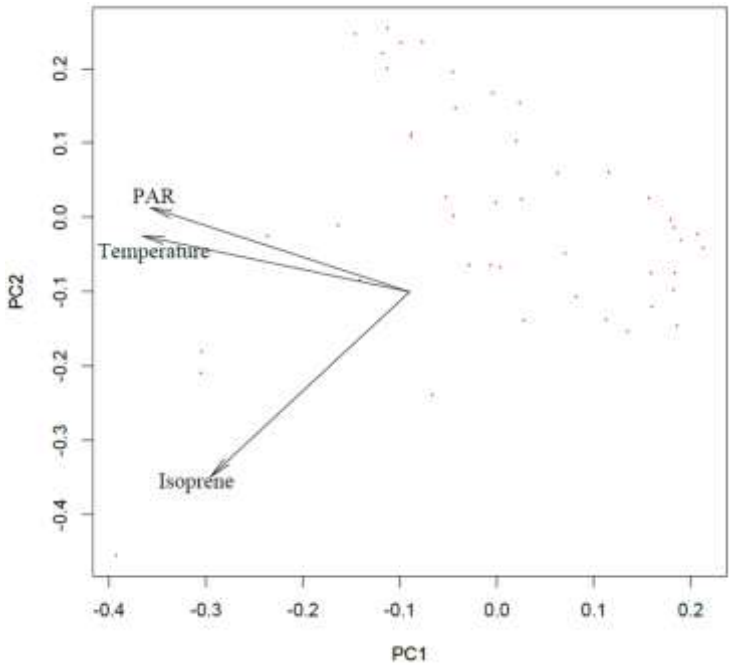

Fig. 3: PCA analysis for isoprene, temperature and light intensity (PAR).

Effect of temperature and light intensity: Isoprene emissions are thought to be dependent on light intensity and not on temperature[7]. In this study, the isoprene emitted by *O. sativa* increased when the temperature and light intensity increased. For example, isoprene was emitted at low levels (~<0.23 ppb) during the night when the temperature is ~25 °C, but when the light intensity and temperature increased towards midday (1100-1400), the isoprene emissions increased significantly.

There was a clear correlation between temperature and isoprene with $r^2 = 0.57$, $p=0.02$, while light intensity and isoprene also showed correlation with $r^2 = 0.84$, $p<0.01$. The results of PCA show that the first principal component alone already accounted for 72.4% of the total variance of the data set. Significant variable loadings for PC1 were positive for isoprene, light and temperature indicating both light and temperature are affecting isoprene concentrations as shown in figure 3.

This observation can be supported by Redeker et al[26] where their results showed that isoprene emissions respond strongly to temperature and light intensity. Previous studies have suggested two major possibilities to explain light dependence, light-induced activation of the rate-limiting IspS enzyme in the plant leaf via changes in chloroplastic Mg^{2+} concentrations[4,18,28] and light-dependent changes in the availability of the substrate dimethylallyl diphosphate (DMADP)[19].

Table 2
Isoprene emissions from *O. sativa* in this study compared to emissions from various types of plants from previous studies using the G93 Model at a standard condition (30 °C, PAR: 1000 µmol m^{-2} s^{-1}).

Plant Name	Isoprene emission (µg g_{dw}^{-1} h^{-1})
*O. sativa**	0.09 (pre-harvest) 0.02 (post-harvest)
Quercus serrata *Quercus crispula* *Fagus crenata* *Quercus acutissima carruthers* *Quercus glauca* *Quercus myrsinaefolia*[2]	224.21 26.04 0.79 0.18 0.04 0.03
Eucalyptus globulus[11]	69
Eucalyptus botryoides	5.3
Bambusa oldhamii[24]	99.1
Pleioblastus simonii	0.7

* Present study

Comparison of G93 model emission rate from other plants: Isoprene emission rates have frequently been estimated using the G93 model developed by Guenther et al[9]. Using this model, the present study showed the predicted emission rates of isoprene emitted during pre- and post-harvest as 0.09 and 0.02 µg g_{dw}^{-1} h^{-1} respectively.

The emissions of isoprene measured were very similar to those from common plants in the surrounding forest such as *Quercus acutissima carruthers*, *Quercus glauca* and *Quercus myrsinaefolia* as shown in table 2. However, our estimation is much lower than emissions from the bamboo plant *Bambusa oldhamii* measured by Okumura et al[24].

Conclusion

Isoprene concentrations were successfully measured during pre- and post-harvest phases for 37 days over rice (*Oryza. Sativa)* paddy field replica. It is clear from the measurements that *O. sativa* can emit significantly high concentrations of isoprene with maxima values at midday of ~70 ppb and minima at night of ~0.01 ppb. The pre-harvest phase measurements of isoprene were clearly higher compared to the post-harvest phase, suspected to be due to emissions from the leaf of *O. sativa*. Temperature and irradiance have strong influences on isoprene emissions and showed strong correlations with the mixing ratios of isoprene with r^2=0.77, $p<0.01$ and r^2=0.84, $p<0.01$ respectively.

We estimated the isoprene emission rate using the G93 model with results of 0.09 and 0.02 µg g_{dw}^{-1} h^{-1} for pre- and post-harvest respectively. Under low NO_x environments, continuous measurement of isoprene is needed to further our understanding of the photochemistry of isoprene production.

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